

# PATENT SPECIFICATION

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## DRAWINGS ATTACHED

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## (54) ALKALI METAL GENERATING AGENTS AND A GENERATOR FOR THE SAME

(71) We, TOKYO SHIBAURA ELECTRIC COMPANY LIMITED, a Japanese corporate body, of 72 Horikawa-cho, Kawasaki-shi, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to alkali metal generating agents and more particularly to said agents put in a vessel made of electric conductive material so as jointly to form an alkali metal generator.

Alkali metal generating agents heretofore used in forming the photoconductive target or surface of a special tube such as an image pickup tube or photoelectric tube consist of a mixture of a single or plurality of alkali metal salts and a single or plurality of reducing agents. The mixture is received in a vessel made of electric conductive material and perforated with a plurality of small bores to form a generator.

There are selectively used various kinds of alkali metal salts according to the type of a photosensitive layer employed. The known types of said salts include chromates, bichromates, tungstates and molybdenates of sodium, potassium, cesium, lithium and rubidium. And the known types of reducing agents are mainly silicon, zirconium, aluminum and boron.

Such prior art alkali metal generator is previously disposed in the prescribed part of a tube at which there is to be formed a photosensitive layer. When it is required to form said layer, the metal vessel is heated by introduction of current or high frequency induction for reaction between the alkali metal salts and reducing agents so as to release alkali metals. The alkali metal thus released is deposited on the surface of a photoelectric substrate, for example, an antimony film previously conditioned for this purpose by main-

taining a part of the tube at a suitable level of temperature, thereby forming a photo-sensitive layer or surface through a further prescribed process.

The aforementioned metal vessel is fabricated by rolling a thin electric conductive sheet in the transverse direction, to form a hollow cylindrical body, spot welding the superposed edge portions at a plurality of points arranged in the longitudinal direction at a prescribed interval and finally closing up an opening at both ends of the hollow cylindrical body by pressure. The aforesaid spot welding is intended to allow the released alkali metal to be drawn out of the vessel through the gaps formed between the welds.

With the prior art alkali metal generator having the aforesaid arrangement, it is required to heat the generator up to the temperature at which there occurs the exothermic reaction of the above-mentioned mixture in order to release a relatively large amount of alkali metal from a given amount of alkali metal salt used. However, heating of the generator to such high level of temperature leads to a rapid occurrence of reaction, thus presenting difficulties in controlling the amount of alkali metal to be released.

To prevent such rapid occurrence of reaction, the prior art adds tungsten as a buffer agent to mixture of alkali salts and reducing agents. However, even addition of said tungsten failed reliably to control the aforementioned rapid reaction. Accordingly, a photo-sensitive layer obtained by the prior art could not display a desired degree of photosensitivity, nor was fully satisfactory in other respects.

It is accordingly the object of the present invention to provide an alkali metal generating agent capable of easily controlling the velocity of exothermal reaction which raised a problem with the prior art, by adding niobium as a reducing agent to the alkali

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metal salt and forming a photosensitive layer or surface having excellent properties and also an alkali metal generator prepared by putting said generating agent in a vessel made of electric conductive metal. The alkali metal salt is suitably one of the formula  $M_2XO_4$ , wherein M is an alkali metal atom, e.g. sodium, potassium or cesium, and X is chromium, tungsten or molybdenum.

10 The composition of the invention will generally take the form of a mixture of the finely divided alkali metal salt and the finely divided niobium.

This invention can be more fully understood from the following detailed description when taken in connection with reference to the accompanying drawings, in which:

15 Figs. 1A and 1B are diagrams comparing the amount of alkali metal released from the prior art alkali metal generating agents corresponding to the associated temperature with that of a similar agent according to an embodiment of the present invention;

20 Figs. 2A to 2C illustrate the effect on reproducibility of the ratio in which there are blended the components of said agent;

25 Figs. 3A and 3B are similar diagrams to Fig. 1A comparing the alkali metal generating property associated with Example D of the invention with those of the prior art alkali metal generating agents;

30 Fig. 4 is a diagram indicating the relationship between the blending ratio of an alkali metal salt and niobium constituting the generating agent used in said Example D and the temperature required for said generation;

35 Figs. 5A and 5B are similar diagrams to Figs. 3A and 3B associated with the alkali metal generating agent of Example E;

40 Fig. 6 is a similar diagram to Fig. 4 associated with Example E;

Figs. 7A and 7B are similar diagrams to Figs. 5A and 5B associated with the alkali metal generating agent of Example F;

45 Fig. 8 is a similar diagram to Fig. 6 associated with Example F; and

50 Fig. 9 is a perspective view, with part broken away, of an example of an alkali metal generator filled with the generating agent of the invention.

For better understanding of the present invention, there will now be described the prior art reducing agents. Reaction of the prior art reducing agents such as silicon, aluminium and zirconium with alkali metal salts is of exothermic type. Among said reducing agents, silicon causes a tremendous evolution of heat. And all these reactions, except between cesium chromate and zirconium, take place very rapidly. Even addition, as heretofore attempted, of powdered tungsten as a

buffer agent for suppressing the above-mentioned rapidity of reaction fails to control reaction velocity with respect to other alkali metal generating agents than a mixture of zirconium and potassium chromate. Although a mixture of zirconium and alkali metal salts allows its reaction velocity to be appreciably controlled as described above, there will most likely take place an explosion during reaction, so that said mixture is barred from use. Where the aforementioned both components are slowly mixed dry in the forming of relatively coarse powders, said explosion may be avoided to a certain extent. However, such process does not afford uniform mixing, nor does use of coarse powders assist in the reduction of the surface area of zirconium taking part in reaction. Accordingly, if it is desired to generate a prescribed amount of alkali metal, it is necessary to use a large amount of the aforesaid mixture. On the other hand, wet mixing of zirconium and alkali metal salts can indeed prevent the occurrence of an explosion. But the alkali metal salt is dissolved in water to become useless. Even where alcohol is used in place of water, minute amounts of water contained in the alcohol denature the alkali metal salt and the segregation of said salt in the subsequent drying process reduces the uniformity of said mixture, thus failing to form a satisfactory photosensitive layer.

The prior art alkali metal generator is generally preheated to minimize the evolution, during reaction, of unnecessary gases from the alkali metal salts, reducing agents and metal vessel used. However, said preheating has the drawback that there are evolved during reaction different amounts of such unnecessary gases from a mixture of an alkali metal salt and silicon or zirconium, depending on the condition in which said preheating is conducted.

Heretofore, there has been further proposed a different type of an alkali metal generator capable of generating appreciable amounts of alkali metal at relatively low temperature, wherein there are added powders of tungsten and boron to a mixture of alkali metal salts and reducing agents. Even this generator, however, presents difficulties in controlling reaction velocity.

The different properties of the prior art alkali metal generating mixture and the mixture of the present invention which typically consists of alkali metal salts and niobium are presented in Figs. 1A and 1B and Table 1 below. The ordinate of the figures represents the amount of alkali metal generated (the ordinate of Fig. 1A denotes cesium and that of Fig. 1B potassium) and the abscissa indicates heating temperature ( $^{\circ}\text{C}$ ).

TABLE 1

Mixture	Mixing ratio	Photosensitivity	Generated state	Temperature of generation
Nb+Cs <sub>2</sub> CrO <sub>4</sub>	2:1	100 μA/lm	Very stable	About 780°C
Si+Cs <sub>2</sub> CrO <sub>4</sub>	2:1	50 μA/lm	Unstable	About 900°C
Zr+Cs <sub>2</sub> CrO <sub>4</sub>	2:1	60 μA/lm	Stable	„
Nb+K <sub>2</sub> CrO <sub>4</sub>	2:1	—	Very stable	About 800°C
Si+K <sub>2</sub> CrO <sub>4</sub>	2:1	—	Unstable	About 900°C
Zr+K <sub>2</sub> CrO <sub>4</sub>	2:1	—	Stable	„
Si+K <sub>2</sub> CrO <sub>4</sub> +W	2:1	—	„	„
Zr+K <sub>2</sub> CrO <sub>4</sub> +W	2:1	—	„	„

Mixture	Puncture or breakage by melting	Generated state affected by varying preheating conditions	Gas evolution before generation of alkali metal
Nb+Cs <sub>2</sub> CrO <sub>4</sub>	Never	Little affected	Very small
Si+Cs <sub>2</sub> CrO <sub>4</sub>	Sometimes	Noticeably affected	Prominent
Zr+Cs <sub>2</sub> CrO <sub>4</sub>	Quite rare	Affected	Fairly noticeable
Nb+K <sub>2</sub> CrO <sub>4</sub>	Never	Little affected	Very small
Si+K <sub>2</sub> CrO <sub>4</sub>	Sometimes	Noticeably affected	Prominent
Zr+K <sub>2</sub> CrO <sub>4</sub>	Quite rare	Affected	Fairly noticeable
Si+K <sub>2</sub> CrO <sub>4</sub> +W	Sometimes	„	Prominent
Zr+K <sub>2</sub> CrO <sub>4</sub> +W	Quite rare	„	Prominent

Mixture	Control of generated state	Getter action of reductant	True density (g/cm³)	Bulk Denisty (g/cm³)
Nb+Cs <sub>2</sub> CrO <sub>4</sub>	Easy	Great	6.42	2.4
Si+Cs <sub>2</sub> CrO <sub>4</sub>	Difficult	Small	2.745	0.9
Zr+Cs <sub>2</sub> CrO <sub>4</sub>	Fairly easy	Great	5.52	1.8
Nb+K <sub>2</sub> CrO <sub>4</sub>	Easy	"	5.07	2.1
Si+K <sub>2</sub> CrO <sub>4</sub>	Difficult	Small	2.45	0.9
Zr+K <sub>2</sub> CrO <sub>4</sub>	Fairly easy	Great	4.44	1.2
Si+K <sub>2</sub> CrO <sub>4</sub> +W	"	Small	11.95	3.1
Zr+K <sub>2</sub> CrO <sub>4</sub> +W	"	Great	8.75	2.1

Mixture	Addition of buffer agent	Possibility of explosion	Yield of alkali metal
Nb+Cs <sub>2</sub> CrO <sub>4</sub>	Unnecessary	None	About 80%
Si+Cs <sub>2</sub> CrO <sub>4</sub>	Necessary	None	About 30%
Zr+Cs <sub>2</sub> CrO <sub>4</sub>	Preferred	Present	About 50%
Nb+K <sub>2</sub> CrO <sub>4</sub>	Unnecessary	None	About 80%
Si+K <sub>2</sub> CrO <sub>4</sub>	Necessary	"	About 30%
Zr+K <sub>2</sub> CrO <sub>4</sub>	Preferred	Present	About 50%
Si+K <sub>2</sub> CrO <sub>4</sub> +W	Already contained	None	About 30%
Zr+K <sub>2</sub> CrO <sub>4</sub> +W	"	Present	About 45%

Table 1 above does not include an alkali metal generating agent containing aluminium as a reducing agent. Such generating agent resembles those containing silicon and zirconium in respect of property, but evolves tremendous amounts of gas during reaction, failing to provide a good photosensitive layer. On the other, use of scale-like pieces of aluminium can indeed suppress gas evolution to a certain extent, but there is required an extra process of working aluminium itself into such scale-like pieces.

There will now be described the present invention in greater detail. It is preferred that powders of alkali metal salts and those of niobium filled into a vessel made of electric conductive metal from which alkali metal is released be mixed in the ratio by weight ranging from 1:0.1 to 8. The reason is that

in the ratio of 1:less than 0.1, the content of niobium is too small to display its expected effect, whereas in the ratio of 1: more than 8, there likely takes place a rapid exothermic reaction. Further speaking of the effect caused by the content of niobium,

(A) Where the alkali metal salt consists of potassium chromate (K<sub>2</sub>CrO<sub>4</sub>), it is advisable to mix it with niobium in the ratio by weight of about 1:0.1 to 8 (or in the mol ratio of about 1:0.23 to 18.4), preferably in the ratio by weight of about 1:0.3 to 4 (or in the mol ratio of about 1:0.69 to 9.2). The mol number of alkali metal represents that of salts thereof. Hereinafter, the mol number of alkali salts is expressed by drawing a bar above symbols representing alkali elements, as  $\bar{Na}$ ,  $\bar{K}$ ,  $\bar{Cs}$ . The mol number of, for example, Na<sub>2</sub>CrO<sub>4</sub> or K<sub>2</sub>WO<sub>4</sub>, is denoted as  $\bar{Na}$  or  $\bar{K}$ .

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- This is derived from the fact that where there was manufactured a photoclectric tube using an alkali metal generating agent whose components were mixed in the former ratio, the yield of alkali metal accounted for about 90 to 100 per cent and in the case of the latter mixing ratio approximately 100 per cent.
- (B) Where the alkali metal salt consists of cesium chromate ( $Cs_2CrO_4$ ), it is desired that said salt be mixed with niobium in the ratio by weight of about 1:0.3 to 10 (or in the mol ratio of about 1:1.21 to 40.49), preferably in the ratio by weight of about 1:0.5 to 3 (or in the mol ratio of about 1:2.02 to 12.12).
- (C) In case sodium chromate is used as an alkali metal salt, the advisable ratio by weight of said salt to niobium is about 1:0.1 to 10 (or about 1:0.19 to 19 in the mol ratio).
- There was formed a photosensitive layer from the aforesaid alkali metal salts, i.e., potassium chromate, cesium chromate and sodium chromate mixed with niobium in varying proportions, the yield of alkali metal being presented in Figs. 2A, 2B and 2C respectively. Throughout these figures, the ordinate represents the percentage yield of alkali metal or reproducibility (Number of good products/Number of tests x 100) and the abscissa denotes the ratio by weight of niobium to the aforementioned alkali metal salts.
- As described above and indicated in Table 1, the alkali metal generator of the present invention allows alkali metal to be released at a temperature about 100°C lower than required for the prior art, reduces the evolution of unnecessary gas, eliminates the necessity of using any special buffer agent and easily controls reaction velocity because reaction does not occur rapidly. Moreover, the generated state of alkali metal does not widely vary with changes in the conditions in which preheating is conducted prior to application of heat for reaction, and on this account, too, reaction velocity can be easily controlled. The fact that the photosensitive layer prepared
- from the alkali metal generating agent of the present invention is elevated about 7G per cent in photosensitivity over the prior art layer evidently proves that said agent is prominently excellent with respect to the aforementioned requirements.
- The alkali metal generator of the present invention further offers the undermentioned favourable effect. The alkali metal generating agent of the invention generally has a greater bulk density than the prior art agent (for example, where the alkali metal salt consists of cesium chromate and there is added niobium thereto as claimed in the present invention, the entire mass has a bulk density of 2.4 g/cm<sup>3</sup>, whereas the prior art agent containing silicon amounts to 0.9 g/cm<sup>3</sup> in bulk density and that containing zirconium to 1.8 g/cm<sup>3</sup>). This means that the alkali metal generating agent of the present invention has a bulk density about 2.5 times that of the prior art silicon-bearing agent and about 1.3 times that of the prior art zirconium-containing agent. Accordingly, the alkali metal generating agent of the present invention can be reduced in bulk, permitting a vessel of electric conductive metal to be made compact. Also the fact that relatively small amounts of said alkali metal generating agent are used and reaction can proceed at a relatively low temperature naturally decreases the evolution of unnecessary gas during the exothermic reaction. Furthermore, the present alkali metal generating agent enables alkali metal to be released in a prominently elevated yield. Though the reason is not fully understood, it is assumed that the intermediate product probably formed by reaction between niobium and the alkali metal generating agent is less liable to obstruct the release of alkali metal than the intermediate product supposed to occur during the reaction of the prior art alkali metal generating mixture.
- For illustration of other combinations of alkali metal salts and niobium, there were prepared four samples from potassium tungstate ( $K_2WO_4$ ) and niobium mixed in different ratios as given below.

Sample	Ratio by weight of Nb to $K_2WO_4$	Mol ratio of K to Nb
a	0.33 : 1	2 : 1.17
b	1 : 1	2 : 3.5
c	3 : 1	2 : 10.5
d	9 : 1	2 : 31.5

In any of the above ratios, the present invention displayed its claimed effect of easily controlling reaction velocity and realizing the initial generation of alkali metal at a temperature of about 700°C.

A further combination of alkali metal salts and niobium wherein there were mixed sodium molybdenate ( $\text{Na}_2\text{MoO}_4$ ) and niobium in the mol ratio  $\bar{\text{Na}}/\text{Nb}$  of 2 to 0.07 exhibited the same effect as described above.

In addition to the aforementioned kinds of alkali metal salts involved in the alkali metal generating agents according to the present invention, there may be used others alone or in combination. Said other salts can still display the same effect as mentioned above. There will now be described the concrete examples where there were used said other salts in combination.

(D) There is used a mixture of sodium and potassium salts as a source of alkali metal. The respective salts are mixed in such a manner that the mol ratio of the total amount of sodium and potassium salts constituting said source to the niobium is about 1:0.2 to 50 [ $(\bar{\text{Na}} + \bar{\text{K}})/\text{Nb} = 0.02$  to 5)]. It is also experimentally disclosed that when the mol ratio of sodium and potassium is  $\bar{\text{Na}}/\bar{\text{K}} = 0.1$  to 10 the resultant photosensitive layer has good photosensitivity.

(E) There are mixed salts of cesium and potassium to form a source of alkali metal in such a manner that the mol ratio of the total amount of cesium and potassium salts constituting said source to the niobium is about 1:0.2 to 100 [ $(\bar{\text{Cs}} + \bar{\text{K}})/\text{Nb} = 0.01$  to 5)]. In this case, the cesium and potassium mixed in the mol ratio of 1:0.05 to 10 ( $\bar{\text{Cs}}/\bar{\text{K}} = 0.1$  to 20) affords good results.

(F) There are mixed salts of cesium and sodium as a source of alkali metal in such a manner that the mol ratio of the total amount of cesium and sodium salts constituting said source to the niobium is about 1:0.125 to 100 [ $(\bar{\text{Cs}} + \bar{\text{Na}})/\text{Nb} = 0.01$  to 8)]. In this case, too, the mixing of cesium and sodium in the mol ratio of 1:0.03 to 10 ( $\bar{\text{Cs}}/\bar{\text{Na}} = 0.1$  to 30) displays a good effect.

The aforementioned metal salts used as a source of alkali metal include, for example, chromates, bichromate, tungstates and molybdates.

The present invention will be more fully understood from the examples which follow:

The powdered materials used in the

Examples had the following average particle sizes.

Niobium	10 microns	
Potassium Chromate	6 microns	
Sodium Chromate	3 microns	
Caesium Chromate	4 microns	60
Tungsten	3 microns	
Silicon	40 microns	
Zirconium	50 microns	
Sodium molybdate	6 microns	
Potassium tungstate	5 microns	65

#### EXAMPLES A, B AND C

There were mixed powders of cesium chromate, potassium chromate and sodium chromate respectively with powders of niobium in the mol ratio of 1:2 to form an alkali metal generating agent. The properties of these mixtures are presented in Figs. 1A and 1B, Figs. 2A to 2C, and Tables 1 and 2.

#### EXAMPLE D

There were mixed powders of sodium chromate and potassium chromate in such a manner that the mol ratio of sodium to potassium was  $\bar{\text{Na}}/\bar{\text{K}} = 1$ . Further, the mixture and powders of niobium were mixed in the mol ratio of  $(\bar{\text{Na}} + \bar{\text{K}})/\text{Nb} = 0.2$  to form an alkali metal generating agent.

For comparison with the aforementioned generating agent of the present invention, there was prepared a reference alkali metal generating agent by adding silicon and zirconium respectively in amounts equal to the aforesaid mol ratio of niobium to the above-described mixed powders of sodium chromate and potassium chromate. The alkali metal generating agents of the present invention and prior art were respectively charged into a perforated vessel made of electric conductive metal to form a photosensitive layer or surface. With respect to the above-mentioned three kinds of mixtures including the alkali metal generating agent of the present invention containing niobium and the reference generating agents containing silicon and zirconium respectively, there was investigated the generated state of sodium and potassium corresponding to the temperature at which said three generating agents were heated, the results being given in Figs. 3A and 3B. There are further presented in Table 2 below comparative data on said three mixtures, the condition of a layer during formation and its properties after formation.

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TABLE 2

Alkali metal generating agent	$\text{Nb} + \text{Na}_2\text{CrO}_4 + \text{K}_2\text{CrO}_4$	$\text{Si} + \text{Na}_2\text{CrO}_4 + \text{K}_2\text{CrO}_4$	$\text{Zr} + \text{Na}_2\text{CrO}_4 + \text{K}_2\text{CrO}_4$
Mol ratio of components	$\bar{\text{Na}}/\bar{\text{K}} = 1$ $(\bar{\text{Na}} + \bar{\text{K}})/\text{Nb} = 0.2$	$\bar{\text{Na}}/\bar{\text{K}} = 1$ $(\bar{\text{Na}} + \bar{\text{K}})/\text{Si} = 0.2$	$\bar{\text{Na}}/\bar{\text{K}} = 1$ $(\bar{\text{Na}} + \bar{\text{K}})/\text{Zr} = 0.2$
Photosensitivity $\mu\text{A}/\text{lm}$ (n:number of sample)	100 (n = 5)	70 (n = 5)	80 (n = 5)
Generated state	Very stable	Unstable	Stable
Temperature of generation $^{\circ}\text{C}$	About 780	About 900	About 900
Puncture or breakage by melting	Never	Sometimes	Quite rare
Generated state affected by varying preheating conditions	Little affected	Noticeably affected	Affected
Gas evolution before generation of alkali metal	Very small	Prominent	Fairly noticeable
Control of generated state	Easy	Difficult	Fairly easy
Getter action of reductant	Great	Small	Great
Bulk density	2.4	0.9	1.8
Addition of buffer agent	Unnecessary	Necessary	Preferred
Possibility of explosion	None	None	Present
Yield of alkali metal	High	Low	Medium

When there was added to the alkali metal generating agent of the present invention used in this example about 10 per cent by weight of tungsten or aluminium oxide on the basis of the total amount of said agent, the generation of alkali metal or reaction velocity was better controlled.

There was further investigated the temperature of generation using the same mater-

ials (mixture of sodium and potassium) as used in this Example D with the mol ratio of niobium to said mixture varied. The results are presented in Fig. 4 wherein the ordinate denotes the temperature  $^{\circ}\text{C}$  required for the generation of alkali metal and the abscissa represents the mol ratio of niobium to said mixture.

**EXAMPLE E**

There were mixed powders of cesium chromate and potassium chromate in such a manner that the cesium and potassium contained therein had a mol ratio of  $\bar{Cs}/\bar{K} = 4$ .  
 5 To said mixture were further added powders of niobium in the mol ratio of  $(\bar{Cs} + \bar{K})/\bar{Nb} = 0.1$  to form an alkali metal generating agent according to the present invention. Next for  
 10 comparison, there were prepared reference alkali metal generating agents corresponding to the prior art agent, using silicon and zirconium respectively as a reducing agent in

place of niobium with all the components mixed in the same mol ratio as is used in the present invention. There was investigated the amount of cesium and potassium generated from said three kinds of generating agents containing niobium, silicon and zirconium respectively, the data on cesium and potassium being presented in Figs. 5A and 5B respectively. There were also tested the properties of a photosensitive layer prepared from these three kinds of generating agents, the results being given in Table 3 below.

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TABLE 3

Alkali metal generating agent	$Nb + Cs_2CrO_4 + K_2CrO_4$	$Si + Cs_2CrO_4 + K_2CrO_4$	$Zr + Cs_2CrO_4 + K_2CrO_4$
Mol ratio of components	$\bar{Cs}/\bar{K} = 4$ $(\bar{Cs} + \bar{K})/\bar{Nb} = 0.1$	$\bar{Cs}/\bar{K} = 4$ $(\bar{Cs} + \bar{K})/\bar{Si} = 0.1$	$\bar{Cs}/\bar{K} = 4$ $(\bar{Cs} + \bar{K})/\bar{Zr} = 0.1$
Photosensitivity $\mu A/lm$ (n:number of sample)	100 (n = 5)	70 (n = 5)	80 (n = 5)
Generated state	Very stable	Unstable	Stable
Temperature of generation $^{\circ}C$	About 780	About 900	About 900
Puncture or breakage by melting	Never	Sometimes	Quite rare
Generated state affected by varying preheating conditions	Little affected	Noticeably affected	Affected
Gas evolution before generation of alkali metal	Very small	Prominent	Fairly noticeable
Control of generated state	Easy	Difficult	Fairly easy
Getter action of reductant	Great	Small	Great
Bulk density	2.4	0.9	1.8
Addition of buffer agent	Unnecessary	Necessary	Preferred
Possibility of explosion	None	None	Present
Yield of alkali metal	High	Low	Medium

There is further indicated in Fig. 6 the temperature required for generation of cesium and potassium with respect to the mixing ratio of Nb to  $\bar{Cs} + \bar{K}$ . In this figure, the ordinate 5 denotes the temperature required for generation of said alkali metals and the abscissa represents the mol ratio of Nb to  $\bar{Cs} + \bar{K}$ .

**EXAMPLE F**

There were mixed powders of cesium 10 chromate ( $Cs_2CrO_4$ ) and sodium chromate ( $Na_2CrO_4$ ) in mol ratio of  $\bar{Cs}/\bar{Na}=3$ . To this mixture was added niobium in the mol ratio of  $(\bar{Cs} + \bar{Na})/Nb=1$  to form an alkali

metal generating agent according to the present invention. There were also prepared prior art generating agents containing silicon and zirconium respectively in the same manner as in Example E. Data of comparative study on the alkali metal generating agents of the present invention and prior art are given in Figs. 7A and 7B and Table 4 below formed in the same arrangement as used in Figs. 5A and 5B and Table 3 respectively. The temperature of generation associated with Figs. 7A and 7B is presented in Fig. 8 formed in the same arrangement as in Fig. 6.

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TABLE 4

Alkali metal generating agent	Nb + $Cs_2CrO_4$ + $Na_2CrO_4$	Si + $Cs_2CrO_4$ + $Na_2CrO_4$	Zr + $Cs_2CrO_4$ + $Na_2CrO_4$
Mol ratio of components	$\bar{Cs}/\bar{Na}=3$ $(\bar{Cs} + \bar{Na})/Nb=1$	$\bar{Cs}/\bar{Na}=3$ $(\bar{Cs} + \bar{Na})/Si=1$	$\bar{Cs}/\bar{Na}=3$ $(\bar{Cs} + \bar{Na})/Zr=1$
Photosensitivity $\mu A/lm$ (n:number of sample)	100 (n = 5)	70 (n = 5)	80 (n = 5)
Generated state	Very stable	Unstable	Stable
Temperature of generation °C	About 780	About 900	About 900
Puncture or breakage by melting	Never	Sometimes	Quite rare
Generated state affected by varying preheating conditions	Little affected	Noticeably affected	Affected
Gas evolution before generation of alkali metal	Very small	Prominent	Fairly noticeable
Control of generated state	Easy	Difficult	Fairly easy
Getter action of reductant	Great	Small	Great
Bulk density	2.4	0.9	1.8
Addition of buffer agent	Unnecessary	Necessary	Preferred
Possibility of explosion	None	None	Present
Yield of alkali metal	High	Low	Medium

- An alkali metal generating agent according to the invention may be prepared by adding another alkali metal salt to the aforesaid combination of alkali metal salts and Niobium.
- 5 There will now be described a concrete example of this case.

There were mixed powders of cesium chromate ( $\text{Cs}_2\text{CrO}_4$ ), potassium chromate ( $\text{K}_2\text{CrO}_4$ ) and sodium chromate ( $\text{Na}_2\text{CrO}_4$ ) in such a manner that  $\bar{\text{Cs}}$ ,  $\bar{\text{K}}$  and  $\bar{\text{Na}}$  are contained in the mol ratio of 1:1:1. To said

mixture was further added niobium in the mol ratio of  $(\bar{\text{Cs}} + \bar{\text{K}} + \bar{\text{Na}})/\text{Nb} = 0.2$  to form an alkali metal generating agent according to the present invention. There were comparatively studied the properties of said agent consisting of only one alkali metal and niobium, namely,



the results being presented in Table 5 below. 20

TABLE 5

Alkali metal generating agent	$\text{Nb} + \text{K}_2\text{WO}_4$	$\text{Nb} + \text{NaMoO}_4$	$\text{Nb} + \text{Cs}_2\text{CrO}_4 + \text{K}_2\text{CrO}_4 + \text{Na}_2\text{CrO}_4$
Mol ratio of components	$\bar{\text{K}}/\text{Nb} = 0.2$	$\bar{\text{Na}}/\text{Nb} = 0.2$	$\bar{\text{Cs}}:\bar{\text{K}}:\bar{\text{Na}} = 1:1:1$ $(\bar{\text{Cs}} + \bar{\text{K}} + \bar{\text{Na}})/\text{Nb} = 0.2 \text{ to } 9.0$
Generated state	Very stable	Stable	Stable
Temperature of generation °C.	700	700	780
Puncture or breakage by melting	Never	Never	Never
Generated state affected by varying preheating condition	Little affected	Little affected	Slightly affected
Gas evolution before generation of alkali metal	Small	Small	Small
Control of generated state	Very easy	Easy	Easy
Addition of buffer agent	Unnecessary	Unnecessary	Unnecessary
Possibility of explosion	None	None	None
Yield of alkali metal	High	Medium	High
Bulk density	2.4	2.4	2.4

As mentioned above, the present invention is characterized in that there is mixed niobium with alkali metal salts. However, there may be further added to said mixture a material, for example, zirconium used as a reducing agent and/or gettering material in the prior

art. There are presented in Table 6 below the properties of a zirconium containing alkali metal generating agent in comparison with those of other agents of the present invention.

TABLE 6

	I	II	III	IV
Alkali metal generating agent	Nb+Si+ Cs <sub>2</sub> CrO <sub>4</sub>	Nb+Si+ K <sub>2</sub> CrO <sub>4</sub> + Na <sub>2</sub> CrO <sub>4</sub>	Nb+Zr+ K <sub>2</sub> CrO <sub>4</sub>	Nb+Si+Zr+W+ Cs <sub>2</sub> CrO <sub>4</sub>
Mol ratio of components	$\bar{C}_s/(Nb+Si) = 0.2$	$(\bar{K}+\bar{Na})/(Nb+Si)$	$\bar{K}/(Nb+Zr) = 0.2$	$\bar{C}_s/(Nb+Si+Zr) = 0.2$
Photosensitivity $\mu A/lm$	100	100	—	100
Generated state	Very stable	Very stable	Very stable	Very stable
Temperature of generation °C	About 780	About 780	About 800	About 780
Puncture or breakage by melting	Quite rare	Quite rare	Never	Quite rare
Generated state affected by varying preheating conditions	Little affected	Little affected	Little affected	Little affected
Gas evolution before generation of alkali metal	Very small	Very small	Very small	Very small
Control of generated state	Easy	Easy	Easy	Easy
Getter action of reductant	Great	Great	Great	Great
Bulk density	2.4	2.0	2.0	3.2
Addition of buffer agent	Unnecessary	Unnecessary	Unnecessary	Unnecessary
Possibility of explosion	None	None	—	—
Yield of alkali metal	About 80%	High	About 80%	About 75%

	V	VI	VII
Alkali metal generating agent	$\text{Si} + \text{Cs}_2\text{CrO}_4$	$\text{Si} + \text{K}_2\text{CrO}_4 + \text{Na}_2\text{CrO}_4$	$\text{Zr} + \text{K}_2\text{CrO}_4$
Mol ratio of components	$\bar{\text{Cs}}/\text{Si} = 0.2$	$(\bar{\text{Na}} + \bar{\text{K}})/\text{Si} = 0.2$	$\bar{\text{K}}/\text{Zr} = 0.2$
Photosensitivity $\mu\text{A}/\text{lm}$	50	70	—
Generated state	Unstable	Unstable	Stable
Temperature of generation $^{\circ}\text{C}$	About 900	About 900	About 900
Puncture or breakage by melting	Sometimes	Sometimes	Quite rare
Generated state affected by varying preheating conditions	Noticeably affected	Noticeably affected	Affected
Gas evolution before generation of alkali metal	Great	Great	Fairly noticeable
Control of generated state	Difficult	Difficult	Fairly easy
Getter action of reductant	Small	Small	Great
Bulk density	0.9	0.9	1.2
Addition of buffer agent	Necessary	Necessary	Preferred
Possibility of explosion	None	None	Present
Yield of alkali metal	About 30%	Low	About 50%

There will now be described by reference to Fig. 9 the case where there is actually prepared a photosensitive layer for a special image pickup tube. Numeral 10 is a vessel made of electric conductive metal. The vessel is prepared by rolling, for example, a thin metal sheet once crosswise into a cylindrical body, and spot welding the longitudinal edge portions at a prescribed interval to form slight gaps or holes 12 between the welds 11. The vessel 10 is filled with an alkali metal generating agent according to the present invention. After the agent is charged, the wall 13 of each end of the vessel is pressed airtight.

There will now be described the case where there was formed the antimony-cesium photosensitive layer of a head-on type photoelectric tube, using two alkali metal generators filled with a generating agent consisting of a mixture of powdered cesium chromate and powdered niobium and a generating agent consisting of a mixture of powdered potassium chromate and powdered niobium respec-

tively. Each mixture weighed 70 mg and the mol ratio of the alkali metal salt to niobium was chosen to be 1:2. To the curved lateral inner surface of a glass bulb having a face plate at the front part were fitted each alkali metal generator and a known antimony generator by so bending them as to correspond to the curvature of said lateral inner surface of the glass bulb. To both ends of each of these fitted generators are connected lead wires drawn to the outside. The preparatory step for forming the aforesaid layer ended by disposing secondary electron multiplying electrodes known to this particular field and an anode at prescribed locations respectively. First, the glass bulb was fully evacuated and then there was introduced current through said antimony generator containing an antimony generating agent. Said agent was heated to a temperature of 520 to 570°C to release antimony so as to deposit a thin film thereof on the inner surface of said face plate to a prescribed thickness. Thereafter, the two

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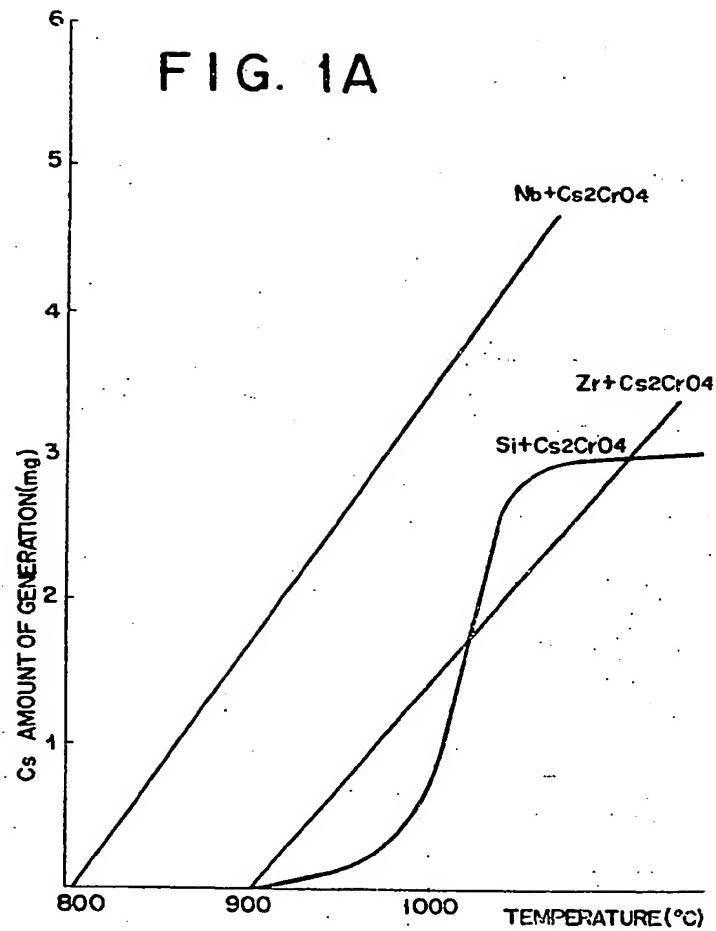
- alkali metal generators of the present invention were preheated 5 minutes at a temperature of 600°C by introducing current therethrough. The generators were further heated 5 to 900°C to release potassium and cesium. Thus, there was deposited a thin cesium-potassium film on said antimony substrate to form a photosensitive layer.
- The photosensitive layer prepared as described above had a photosensitivity of 100  $\mu\text{A}/\text{lm}$ , showing that it had excellent properties.
- There will now be described the formation of a multi-alkali photosensitive layer used in an X-ray fluorescent multiplying tube. There were prepared three mixtures comprising powders of cesium chromate, sodium chromate and potassium chromate each blended with powders of niobium in the mol ratio of 1:2 to form alkali metal generating agents. The mixtures containing cesium and sodium each weighing 250 mg and the mixture containing potassium weighing 200 mg were separately placed in the aforementioned metal vessels to provide alkali metal generators. Each of these generators was put in a known bulb having a fluorescent face formed at one end and a plate of insulating material disposed opposite to said fluorescent face at a close interval. The generators were preheated 5 to 10 minutes at a temperature of 350°C. Then they were heated to 900°C to release each alkali metal so as to form a multialkali photosensitive layer on said insulation plate.
- The resultant photosensitive layers had an excellent photosensitivity of 100  $\mu\text{A}/\text{lm}$  like that of the preceding case.
- WHAT WE CLAIM IS:—**
1. An alkali metal generating agent prepared from a mixture of an alkali metal salt and niobium.
  2. A generating agent according to claim 1 wherein said alkali metal salt and niobium are mixed in the ratio by weight of 1:0.1 to 10.
  3. A generating agent according to claim 1 wherein the alkali metal salt is one selected from potassium tungstate, potassium chromate, cesium chromate, sodium chromate and sodium molybdate.
  4. A generating agent according to claim 3 wherein the alkali metal salt consists of potassium chromate, which is mixed with niobium in the mol ratio of 1:0.23 to 18.4.
  5. A generating agent according to claim 3 wherein the alkali metal salt consists of cesium chromate, which is mixed with niobium in the mol ratio of 1:1.21 to 40.49.
  6. A generating agent according to claim 3 wherein the alkali metal salt consists of sodium chromate, which is mixed with niobium in the mol ratio of 1:0.19 to 19.
  7. A generating agent according to claim 1 wherein the alkali metal salt is one selected from a first mixture comprising sodium salts and potassium salts, a second mixture comprising cesium salts and potassium salts and a third mixture comprising cesium salts and sodium salts.
  8. A generating agent according to claim 7 wherein the alkali metal salt consists of said first mixture, which is mixed with niobium in such a manner that the total amount of sodium and potassium contained in said mixture bears the mol ratio of 1:0.2 to 50 to the niobium.
  9. A generating agent according to claim 8 wherein the molar ratio of sodium to potassium contained in said first mixture is 1:0.1 to 10.
  10. A generating agent according to claim 7 wherein the alkali metal salt consists of said second mixture, which is mixed with niobium in such a manner that the total amount of cesium and potassium contained in said mixture bears the mol ratio of 1:02 to 100 to the niobium.
  11. A generating agent according to claim 10 wherein the molar ratio of cesium to potassium contained in said mixture is 1:0.05 to 10.
  12. A generating agent according to claim 7 wherein the alkali metal salt consists of said third mixture, which is mixed with niobium in such a manner that the total amount of cesium and sodium contained in said mixture bears the mol ratio of 1:0.125 to 100 to the niobium.
  13. A generating agent according to claim 12 wherein the molar ratio of cesium to sodium contained in said third mixture is 1:0.03 to 10.
  14. A generating agent according to claim 1 wherein said alkali metal salt consists of cesium chromate and which further includes silicon.
  15. A generating agent according to claim 1 wherein said alkali metal salt consists of potassium chromate and which further includes silicon.
  16. A generating agent according to claim 1 wherein said alkali metal salt consists of potassium chromate and which further includes zirconium.
  17. A generating agent according to claim 1 wherein said alkali metal salt consists of alkali chromate and which further includes silicon, zirconium and tungsten.
  18. A generating agent according to claim 1 wherein said alkali metal salt consists of a mixture of cesium chromate, potassium chromate and sodium chromate.
  19. An alkali metal generator comprising a vessel made of electric conductive material with a plurality of holes and an alkali metal generating agent prepared from a mixture of an alkali metal salt and niobium.
  20. A generator according to claim 19 wherein said agent is selected from the agents claimed in claim 2 to 18.

21. An alkali metal generating agent, substantially as herein described with reference to the accompanying drawings. 25
- 5 22. An alkali metal generator, substantially as herein described with reference to the accompanying drawings.
23. A method of generating an alkali metal which comprises heating a generating agent as claimed in any one of claims 1—13 and 21 to a temperature at which the alkali metal is released. 30
- 10 24. A method of generating an alkali earth metal which comprises passing an electric current or high frequency electromagnetic radiation through a generator as claimed in any one of claims 19, 20 and 22 to heat the generating agent contained therein to a temperature at which the alkali metal is released. 35
- 15 25. A method as claimed in claim 23 or 20 claim 24 in which the generating agent is heated to a temperature of at least 700°C.
26. A method of forming a film of an alkali metal upon a substrate which comprises generating an alkali metal vapour by a method as claimed in any one of claims 23—25 and depositing this vapour upon the substrate. 40
27. A method as claimed in claim 26 in which the substrate is a tube and the generating agent is heated inside the tube.
28. A method as claimed in claim 23 substantially as hereinbefore described with reference to any of the Examples.
29. A method as claimed in claim 24 substantially as hereinbefore described with reference to any of the Examples.
30. A method as claimed in claim 26 substantially as hereinbefore described with reference to any of the Examples.
31. A substrate when coated with an alkali metal by a process as claimed in either of claims 26 and 27.

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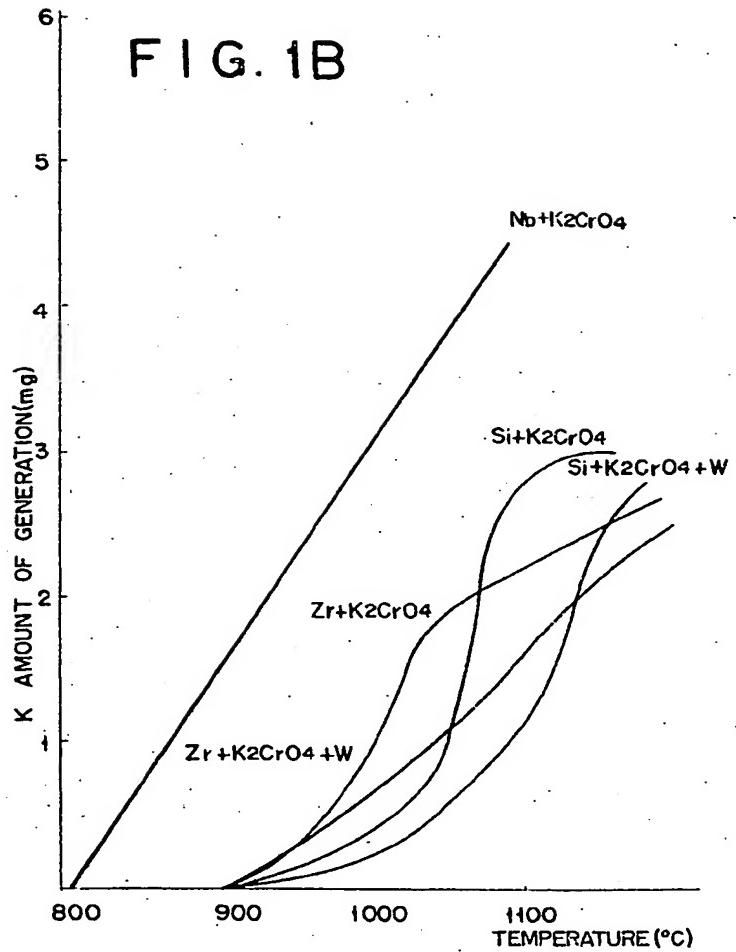


FIG. 2A

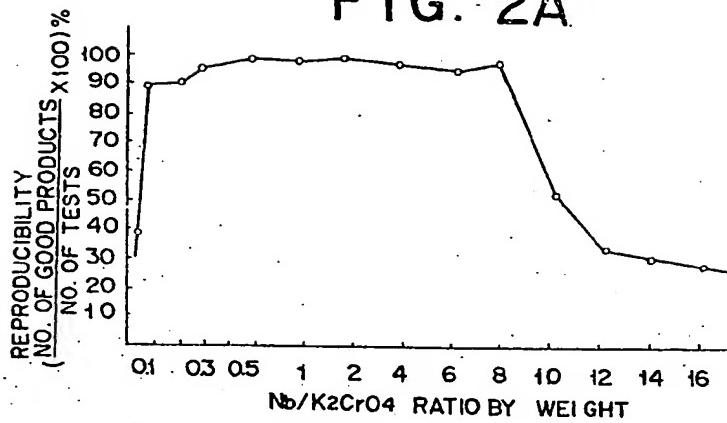
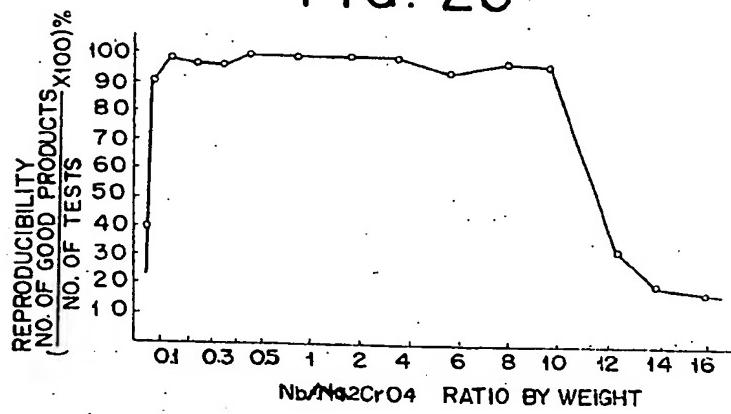
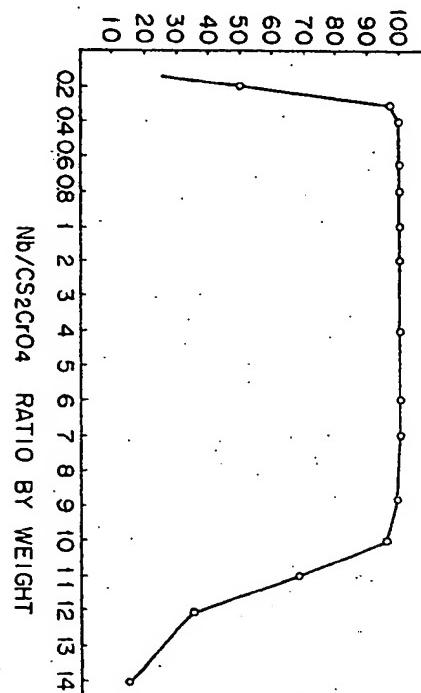


FIG. 2C

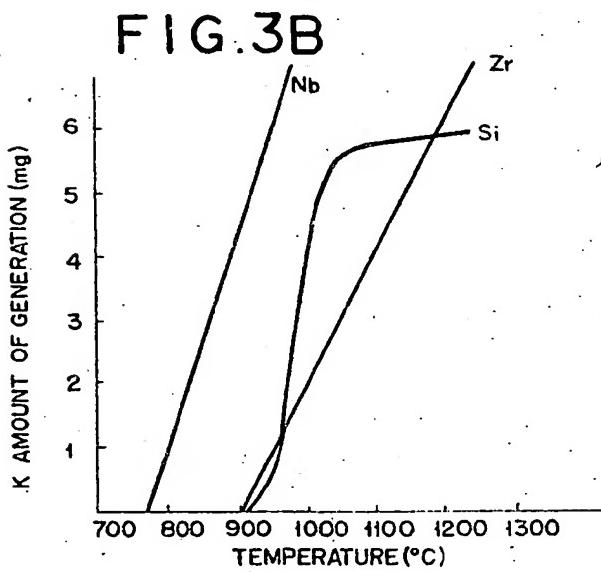
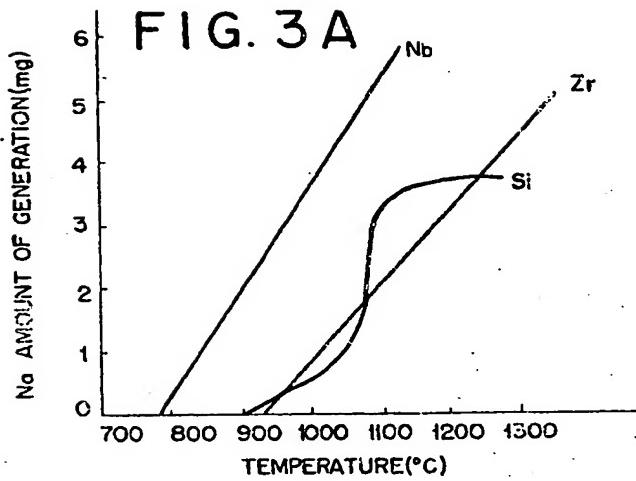


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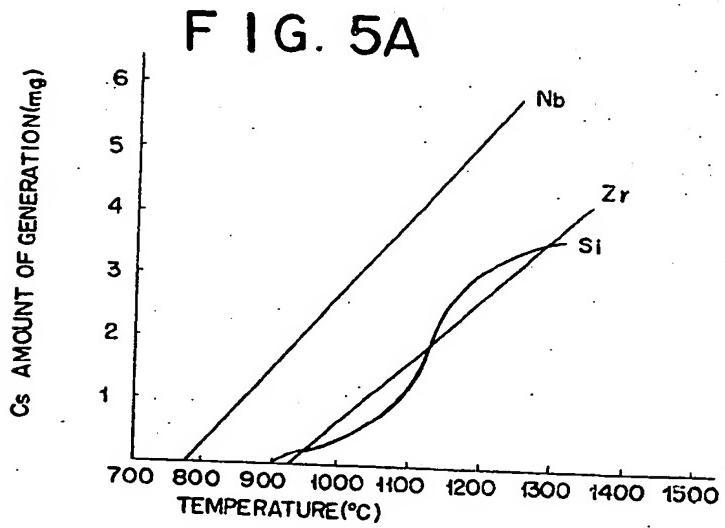
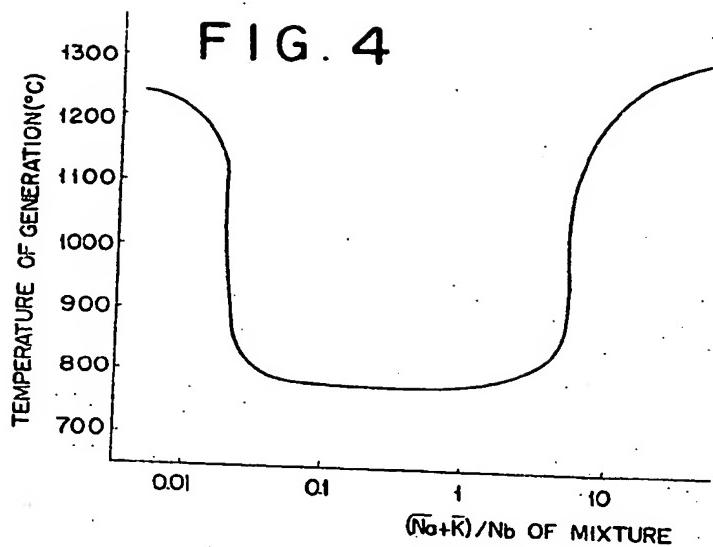
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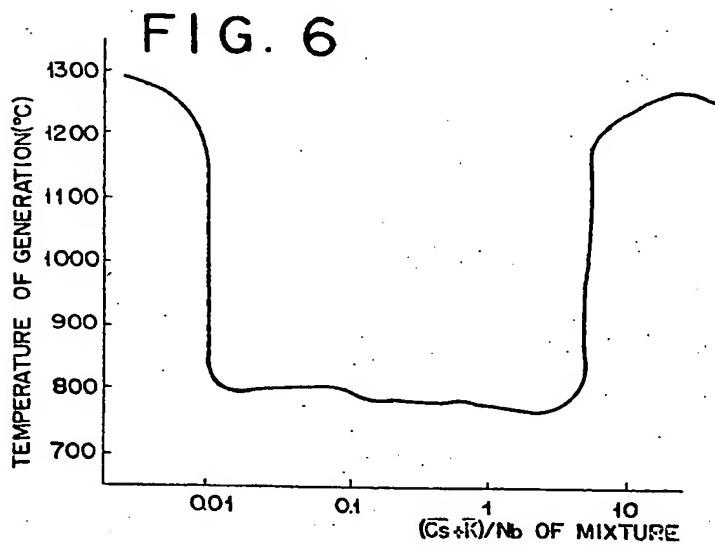
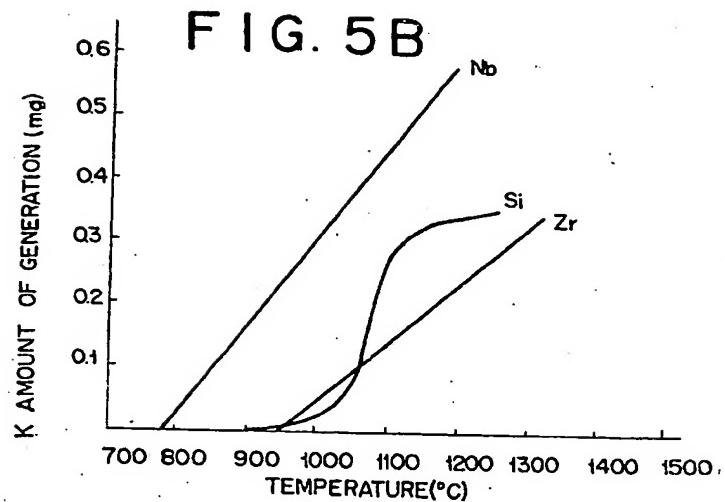


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FIG. 7A

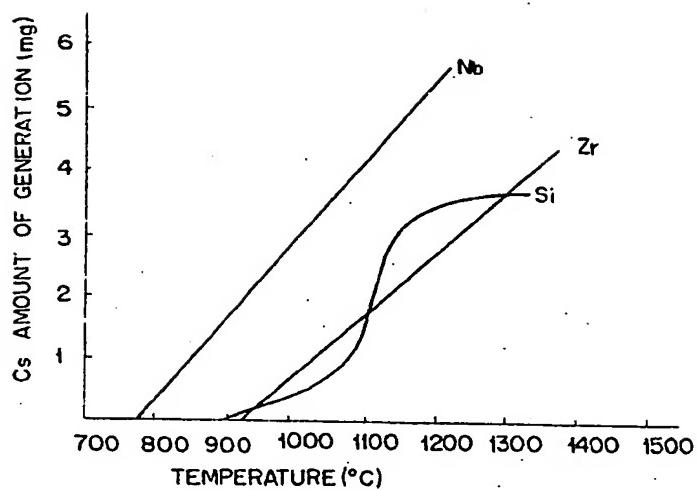
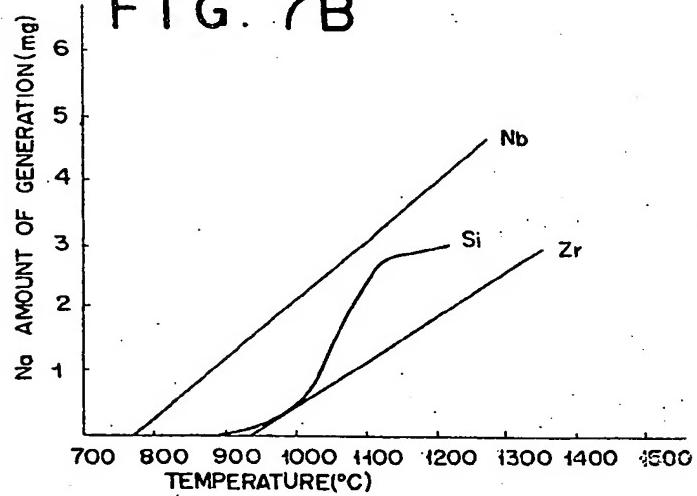


FIG. 7B



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FIG. 8

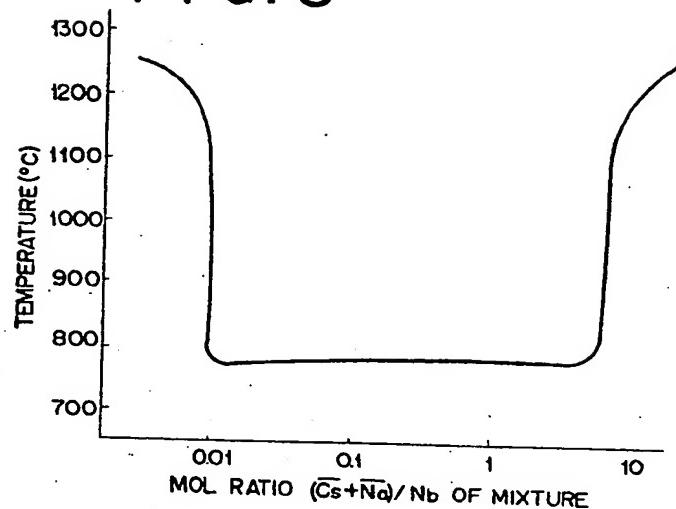


FIG. 9

